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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference xxx	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/PL 03/00065	International filing date *(day/month/year)* 02.07.2003	Priority date *(day/month/year)* 31.10.2002
International Patent Classification (IPC) or both national classification and IPC C23C8/22		
Applicant SECO/WARWICK SP. Z O.O. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 7 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
19.04.2004	23.03.2005
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer Badcock, G Telephone No. +49 89 2399-8445

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/PL 03/00065

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-5 received on 03.12.2004 with letter of 30.11.2004

Claims, Numbers

1 received on 03.12.2004 with letter of 30.11.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1
	No:	Claims	

2. Citations and explanations

see separate sheet

1). Clarity, Art.6 PCT

The method of claim 1 is unclear as the phrase " .. the temperature required for start..." gives no hint as to what temperature the atmosphere of ammonia should be kept and at which the carburizing should start.

The phrase "... introduction of the active nitrogen carrier ..... accompanied by the introduction of ammonia ..." in the method of the claim is unclear, only in terms of the english used, as the active nitrogen carrier is ammonia.

2). Novelty, Art.33(2) PCT and Inventive step, Art.33(3) PCT

The method of claim 1 is novel, as the closest prior art EP-A-0 545 069, does not disclose a method of under pressure carburizing of steel workpieces in a vacuum chamber at the relatively low pressure of 1 to 500 mbar. Rather, it discloses the use of ammonia at much higher pressures of greater than 1 bar between 100-1000°C. Neither is the use of a vacuum chamber mentioned as these pressures are at overpressure. The claimed method parameters may allow nitrogen to diffuse deep into the surface of the steel workpiece, so that no undesireable brittle iron nitrides are formed, and inhibting the growth of grains during the carburizing process.

Method for under-pressure carburizing of steel workpieces

The object of this invention relates to the method for carburizing of steel products, mainly parts of machines, vehicles and all types of mechanical apparatuses, in vacuum furnaces under reduced pressure and elevated temperature.

A method for carburizing of products made of steel in a furnace chamber is known from the US Patent 6,187,111. In this method, vacuum in the range of 1 to 10 hPa is generated and the temperature of the carburizing process is maintained between 900°C and 1100°C. The carbon carrier there is gaseous ethylene. Another US Patent, 5,205,873, describes the carburizing process carried out under low pressure in a furnace chamber heated up to temperatures between 820°C and 1100°C. This process starts in a chamber where an initial vacuum up to 10^{-1} hPa was generated to remove the air. Then, after backfill of the chamber with pure nitrogen, workpieces to be carburized are placed into it. In the loaded chamber, a vacuum in the range of 10^{-2} hPa is generated and the charge is heated up to the austenitizing temperature and this temperature is maintained until the temperatures across the workpiece are equalised; afterwards the furnace chamber is backfilled with hydrogen up to 500 hPa. Then ethylene as the carbon carrier is introduced under the pressure from 10 to 100 hPa and a gas mixture consisting of hydrogen and ethylene is created, in which the ethylene content ranges from 2% to 60% of the gas mixture by volume.

Also the US Patent 5,702,540, describes the method of carburizing, according to which the charge is pre-heated under vacuum and gaseous unsaturated aliphatic hydrocarbons are used as the carbon carrier. This method can also be applied for carbonitriding, where together with the carbon carrier an active nitrogen carrier is introduced to the furnace chamber.

The method for under-pressure carburizing of steel workpieces according to the present invention consists in the introduction of an active nitrogen carrier during heating up of the charge, preferably after the temperature of 400°C is reached. The introduction of the active nitrogen carrier is terminated when the charge reaches the temperature required to start the carburizing process; as soon as this temperature is reached the carbon carrier is added. The pressure in the furnace chamber during a continuous or pulse introduction of the active nitrogen carrier should be maintained within the range of 1 to 500 mbar.

The most preferable and beneficial effects are obtained when the active nitrogen carrier is ammonia and the pressure during its introduction is maintained within the range of 1 to 50 mbar.

The method according to the present invention is distinguished by a possibility of an effective application of the upper range of carburizing temperatures due to restraining the growth of austenite grains as a result of initial saturation of the surface area with nitrogen and in consequence the process is significantly accelerated.

One of possible implementations of the method for under-pressure carburizing of steel workpieces according to the present invention is illustrated by the following examples:

Example 1

A furnace chamber of the size 200x200x400 mm was loaded with workpieces made of low carbon steel grades C15, 16CrMn5 and 17CrNiMo. The total surface area of the charge was 0.4 m^2. After pre-heating under vacuum up to 400°C ammonia was introduced to the furnace chamber interior with a constant flow rate of 50 l/hr. The process atmosphere was maintained under a constant pressure of 5 mbar. When steel workpieces had reached the temperature of 950°C, the introduction of ammonia was interrupted, and carburizing atmosphere was introduced for twenty minutes and a constant temperature of the vacuum furnace chamber was maintained; the atmosphere was made up of the carbon carrier in the

form of a mixture of ethylene and acetylene in the volume ratio 1, mixed with hydrogen in the volume ratio 1,17, introduced with a constant flow rate 190 l/hr and thus generating pressure pulse in the furnace chamber within the range of 3 to 8 mbar. For the next 8 minutes steel workpieces were heated under vacuum at the temperature of 950°C and then slowly cooled under vacuum down to the ambient temperature. On individual steel workpieces carburized layers were produced with the following performance.

Steel grade	Surface carbon concentration [%]	Case depth to limit structure – 50% perlite + 50% austenite [mm]	Original grain size [mm]
C15	0.65	0.40 ± 0.005	40% -0.008 60% -0.011
16CrMn5	0,71	0,46 ± 0,005	50%-0,011 50%-0,013
17CrNiMo	0,72	0,47 ± 0,005	70%-0,011 30%-0,016

The surface of all workpieces after carburizing was clean and bright without any evidence of soot and tar.

Example 2

A furnace chamber of the size 200x200x400 mm was loaded with workpieces made of low carbon steel grades 16CrMn5 and 17CrNiMo. The total surface area of the load was 0.4 m^2. After pre-heating under vacuum up to 400°C ammonia was introduced to the furnace chamber interior with a constant flow rate of 50 l/hr. The process atmosphere was maintained under a constant pressure of 5 mbar. When steel workpieces had reached the temperature of 950°C, the introduction of ammonia was interrupted, and carburizing atmosphere was introduced for twenty minutes and a constant temperature of the vacuum furnace chamber was maintained; the atmosphere was made up of the carbon carrier in the form of a

mixture of ethylene and acetylene in the volume ratio 1, mixed with hydrogen in the volume ratio 1,17 introduced with a constant flow rate 190 l/hr and thus generating pressure pulse in the furnace chamber within the range of 3 to 8 mbar. For the next 20 minutes steel workpieces were heated under vacuum at the temperature of 950°C and then fast cooled down to the ambient temperature under nitrogen at the pressure increased up to 6 bar. On individual steel workpieces carburized layers were produced with the following performance.

Steel grade	Surface hardness [HV_{01}]	Case depth to limit hardness 500 HV_{01}
16CrMn5	744	0,48 ± 0,005
17CrNiMo	820	0,49 ± 0,005

The surface of all workpieces after carburizing was clean and bright without any evidence of soot and tar.

Example 3

A furnace chamber of the size 200x200x400 mm was loaded with workpieces made of low carbon steel grades C15, 16CrMn5 and 17CrNiMo. The total surface area of the load was 0.4 m^2. After pre-heating under vacuum up to 400°C ammonia was introduced to the furnace chamber interior with a constant flow rate of 50 l/hr. The process atmosphere was maintained under a constant pressure of 5 mbar. When steel workpieces had reached the temperature of 1000°C, the introduction of ammonia was interrupted, and carburizing atmosphere was introduced for twenty minutes and a constant temperature of the vacuum furnace chamber was maintained; the atmosphere was made up of the carbon carrier in the form of a mixture of ethylene and acetylene in the volume ratio 1, mixed with hydrogen in the volume ratio 1,17 introduced with a constant flow rate 270 l/hr and thus generating pressure pulse in the furnace chamber within the range of 3 to 8 mbar. For the next five minutes steel workpieces were heated under vacuum at the temperature of 1000°C and then slowly cooled under vacuum down to the ambient

temperature. On individual steel workpieces carburized layers were produced with the following performance.

Steel grade	Surface carbon concentration [%]	Case depth to limit structure – 50% perlite + 50% austenite [mm]	Original grain size [mm]
C15	0.66	0.52 ± 0.005	70% -0.011 30% -0.013
16CrMn5	0,70	0,58 ± 0,005	50%-0,013 50%-0,016
17CrNiMo	0,70	0,59 ± 0,005	60%-0,013 40%-0,016

The surface of all workpieces after carburizing was clean and bright without any evidence of soot and tar.

CLAIMS:

1. The method of under-pressure carburizing of steel workpieces with the introduction of the active nitrogen carrier to the vacuum furnace chamber **is characterized in that** the active nitrogen carrier is introduced during pre-heating of the charge until the charge reaches the carburizing temperature and the pressure in the furnace chamber is maintained within the range of 1 to 500 mbar.
2. The method according to claim 1 **is characterized in that** the said active nitrogen carrier can be introduced to the furnace chamber in a continuous or pulse manner.
3. The method according to claim 1 **is characterized in that** it is most beneficial and preferable if the pressure during the introduction of the said active nitrogen carrier is maintained within the range of 1 to 50 mbar.
4. The method according to claim 1 **is characterized in that** it is beneficial and preferable if the introduction of the said active nitrogen carrier starts once the temperature of the charge reaches 400°C.
5. The method according to claim 1 **is characterized in that** it is most beneficial and preferable if the said active nitrogen carrier is ammonia